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OXYGEN DEFICIENCY IN ANTARCTIC AIR

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[U. S. Antarctic Service, 1939–1941]

Surprising deficiency in oxygen content of the Antarctic atmosphere, too great to be attributable to instrumental technic, was found in the course of a series of measurements made at Little America III (lat. 78°28′ S., long. 163°30′ W.) during 1940 and 1941.

Oxygen-percentage composition of dry air was found to vary between the wide limits of 20.50 volume percent in summer and 20.80 volume percent in winter, thus indicating a possible seasonal change in the deficiency. "Normal" middle latitude value is 20.95 volume percent.

All of the 25 summertime (December and January) analyses presented here gave values between 20.48 and 20.64 volume percent for oxygen, with an average of 20.556.

Of the 12 wintertime (July and August) determinations, 8 fell between 20.69 and 20.76 volume percent, averaging 20.726. Four others, on July 22, fell entirely outside this range, being between 20.48 and 20.54, with an average value of 20.505.

Since this large variation in the wintertime readings is wholly outside the limits of instrumental error (as discussed later), it seems evident that they represent two radically different types of air. Further light may be thrown on this question, and indeed on the entire subject, by later study of the surface weather records and the upper-air observations.

HISTORY

For 30 years the accepted value for the oxygen concentration in the air of temperate latitudes, where most determinations have been made, has been 20.95 volume percent (**1**), but "the second decimal is not certain," as Paneth points out (**2**).

In a more recent paper Carpenter (**3**), after further work in extension of Benedict's classic determinations of 1909–11, concludes that the entire atmosphere up to the tropopause is constant in composition regardless of meteorological effects, and is but slightly affected by large-scale industrial contaminations.

However, Shepherd (**4**) has found, in experiments now in progress, confirmation of earlier work by Morley (**5**) that the oxygen content of polar continental air ("cold waves") is slightly lower than normal. So far as is known, the determinations presented here are the first to be made on the Antarctic Continent itself. However, 10 samples of air obtained by the Charcot expedition of 1908–10 in the Bellingshausen Sea and on the Palmer Land coast, analyzed by Müntz and Lainé (**6**), showed no oxygen deficiency:

> The average of all these results is 20.957. They vary between a minimum of 20.91 and a maximum of 21.00 (volume percent). They are thus comparable to those which Regnault obtained at Paris, where the mean was 20.960, with a minimum of 20.913 and a maximum of 20.990. We must conclude therefore that the air of Antarctic regions contains a proportion of oxygen comparable to that which exists in the climate of France.

Analyses were made in a Regnault eudiometer, modified by Schloesing, of samples collected in the field in glass flasks which were sealed over a gas flame. Carbon dioxide was first removed from the air, and then to the purified air was added a convenient quantity of pure hydrogen and the oxygen computed "by taking one-third of the volume consumed by the combustion."

Four of the samples were obtained in winter quarters on Peterman (Lund) Island (Port Circumcision, 65°11′ S., 64°15′ W.) on the west coast of the Palmer Peninsula, the rest at sea during the cruises of the *Pourquoi Pas.* No correlation between latitude or season can be found in the figures, which agree within the limits of the method used.

However, in the carbon dioxide content, an average of 0.01997 volume percent was obtained (neglecting one poor sample) and the smallest results, 0.01447 and 0.01702, were obtained at the highest latitudes, 69°30′ and 70°05′ S.

> It appears from these figures, in a most striking way that the quantity of carbon dioxide which exists in the air of southern regions is quite noticeably less than that which exists in Europe. We have in effect a mean of 0.0205, while determinations of Müntz and Aubin made in the Northern Hemisphere, in very distant stations, gave them a figure of 0.0282. Their former studies, made at Cape Horn in latitude 55°31′, had already given them a mean of 0.0256, quite clearly inferior to that of the Northern Hemisphere. (**7**).

However, the oxygen analyses of the same Cape Horn air samples, obtained during an astronomical expedition there in 1885, show rather large variations and a general oxygen deficiency. Due to the current state of air analyses, they concluded that their figures showed substantial agreement with determinations elsewhere. (**10**).

No deficiencies have been noted in high northern latitudes. In 1886 three of the foremost gas analyst of the day made determinations of air at Cleveland, Para, Bonn, Dresden and Tromso, and found that "the oxygen content (of the atmosphere) in the neighborhood of the poles was somewhat higher than in the neighborhood of the Equator," (**9**) an extrapolation doubly unjustifiable in that its extension northward is not valid and the Southern Hemisphere cannot be considered identical with the Northern Hemisphere.

Krogh, one of the leading analysts of this century, found average or higher than average oxygen content around Greenland in a first series of determinations, average or slightly lower values in a second series (**10**), and later (**11**) considers the air to be substantially uniform.

In recent years much work has been done in analyses of air from high levels, the general conclusion to date being that convection maintains a uniform composition

at least as high as the tropopause, above which the oxygen content decreases rapidly, dropping to less than 20.00 percent a few kilometers above it.

Most of these studies have been primarily concerned with ozone, but Regener says (**12**):

> The height of the ozone layer in the stratosphere should also be lower in polar regions than in equatorial regions, first, because the oxygen content in polar regions decreases with height more rapidly than in equatorial regions and secondly—which is perhaps of even greater effect—because the greater stability of the atmosphere in polar regions tends to increase the diffusion of the heavy ozone downwards.

Concerning the possible effects of the vertical structure of the atmosphere on the oxygen concentration, it may be pointed out that the tropopause at Little America III was found in the summer at 9 to 10 kilometers but tended to disappear entirely in the winter, a continuous lapse rate being observed to −80° C. at 12 km., the instrumental limit. Surface pressures also are an inch or more (30 to 40 mbs.) lower than the world average.

The physical and biological nature of the Antarctic may have some bearing on the results reported here. Oxygen is constantly being removed from the atmosphere, H. Spencer-Jones points out (**13**), by the weathering of the ferrous oxide of igneous rocks into ferric oxide in sedimentary rocks. "The amount of oxygen withdrawn thus * * * is very considerable," and replenishment is accomplished through the biologic cycle, in which plants liberate oxygen during photosynthesis and processes of decay absorb it. Although "whenever organic matter is buried there is a net gain of oxygen to the atmosphere, it seems probable that * * * if the coal, oil and other organic deposits could be unburied and completely burned, the whole of the oxygen in the atmosphere would be used up."

The Antarctic Continent, while almost devoid of vegetation, has a relative abundance of igneous rocks protruding through its ice cap and subject to intense weathering. Vast unknown areas may have even more mountains than those already explored; of the hundred thousand square miles of hitherto unseen territory explored by the U. S. Antarctic Expedition, more than half was mountainous.

However, most of the rock weathering is mechanical rather than chemical. Although summertime air temperatures lie just below the freezing point, and bare rocks themselves may be actually warm, Wade and Warner (**14**) estimate that only 10 to 15 percent more rock is uncovered to the air in summer than in winter, when temperatures far below zero prevail.

Discussing "The Origin of Atmospheric Oxygen," Nichols (**15**) says oxygen may have been an original constituent of the atmosphere, or may be formed by impact of white-hot planetesimals with water vapor, or released by green plants in photosynthesis, or emitted by volcanic vents. Six other possible sources are offered: Decomposition of water vapor by meteoric material (currently as opposed to in geologic times), or by high upper stratosphere temperatures, or by penetrating radiation; decomposition of stony meteorites which contain oxides; formation of ammonia by lightning or meteors; and formation of hydrochloric acid by free chlorine emitted volcanically. He concludes "The net result of all these reactions on the quantity of oxygen in the atmosphere cannot be evaluated at present."

How these various factors affect the oxygen content of the Antarctic atmosphere, this paper does not venture to say. It is merely to present (table 1) the results of an investigation conducted incidentally to studies in physiology, on the one hand, and in general climatic and aerologic conditions, on the other.

EXPERIMENTAL

Analyses were made during July, August and December of 1940 and January of 1941 at Little America III, the West Base of the U. S. Antarctic Service. This base was on the so-called Ross Ice Shelf some three miles south of the edge at which this thick ice sheet terminates as the Ross Ice Barrier, the southern limit of navigation in the Ross Sea.

It was about 1 mile east of the Bay of Whales and about 7 miles northeast of Little America I and II, the base of the Byrd Antarctic Expeditions of 1928–30 and 1933–35. Ice and snow surround the camp for hundreds of miles in all directions except for the sea to the north. Thus, most of the air analyzed had been in transit over a pure snow surface for some time before collection.

Samples were taken only after wind direction had been generally constant for at least 6 hours and were always obtained to windward of camp to avoid contamination from camp smoke and gases. The air was collected over mercury in a 60 ccm. gas-sampling bottle and was allowed to come to room temperature (since outside temperatures were always below freezing) before analysis in a portable Haldane apparatus (**13**), which is described here briefly.

It consists essentially of five parts: (1), a calibrated measuring burette of 10 ccm. capacity; (2), an absorption pipette filled with potassium hydroxide for carbon dioxide; (3), an absorption pipette filled with alkaline potassium pyrogallate for oxygen; (4), an uncalibrated tube, similar to the measuring burette, called the thermobarometer, for automatic compensation of slight changes in temperature during analysis; and (5), a leveling bulb filled with mercury by which gas samples can be drawn into the apparatus, measured at atmospheric pressure, forced successively into the carbon dioxide absorption pipette, into the measuring burette for determination of the new volume, then into the oxygen absorption pipette and finally into the measuring burette for final volume determination.

Both measuring burette and thermobarometer are contained in a water chamber kept at uniform temperature by stirring. The various parts, joined together by short lengths of heavy-walled rubber tubing, are mounted compactly in a carrying case which becomes a support during use. Communication from the measuring burette to the sample flask and to the absorption pipettes is regulated by several stopcocks. Small portions of acidified water in the thermobarometer and above the mercury in the measuring burette keep the gas sample saturated with water vapor at all times.

Operation of the apparatus, although simple, requires that particular care be given to details to obtain reliable results. Before introduction of the sample, carbon dioxide and oxygen in the apparatus are eliminated by drawing air into the burette and running it alternately into the two absorption pipettes until no further absorption of gas occurs; at this stage the apparatus contains only nitrogen saturated with water vapor.

After this nitrogen has been washed out of the apparatus with several small portions of the sample to be analyzed, a 10 ccm. portion is drawn in and allowed to become saturated. The initial volume is measured, the carbon dioxide removed and the new volume measured; then the oxygen is absorbed and the final volume determined. The two decreases in volume correspond respectively to the carbon dioxide and oxygen contents of the original

dry-air sample. Simple calculations give percentage compositions of the dry constituents.

Thus the figures obtained are absolute values comparable to absolute values determined by other methods in other areas. They represent, however, percentages of only the dry constituents of the original sample. Due to the method of the apparatus, no determination could be made of the amount of water vapor present; no psychrometric observations were made because of the low temperatures prevalent.

As further clarification of the data the following statement from Peters and Van Slyke (**16**) may be quoted:

> In the analysis of moist air by the Haldane method each volume measurement, before or after the absorption of any gas, is made at the same partial pressure of the dry gases. This pressure is $B-W$ (barometric pressure less vapor tension of water). The effect of the vapor tension W is therefore merely to lower the pressure of all volume readings by a constant amount and thereby to increase all volume readings by a constant proportion over what they would be for the dry gases * * *. The results of a gas analysis are therefore independent of temperature, barometric pressure and wet or dry state of the gas, so long as these factors are constant.

TABLE 1.—*Analysis of Antarctic air*

Date	CO_2 volume	O_2 volume	Residual (N_2, A, etc.)	Wind movement: At collection: Direction	Wind movement: At collection: M. p. h.	Wind movement: Past 12 hours	Temperature	Barometer in past 6 hours
Winter-1940:	*Pct.*	*Pct.*					°F.	
July 13	0.06	20.75	79.19	E.	7	S.-E.	−47	Very steady.
	.07	20.76	79.17					
22	.06	20.54	79.40	E.	10	E.	−28	Rising fast.
	.07	20.51	79.42					
22*	.07	20.48	79.45	E.	10	E.	−27	Rising fast.
	.09	20.49	79.42					
29	.03	20.73	79.24	E.	13	E.-SE.-E.	−14	Very steady.
	.06	20.73	79.21					
29*	.03	20.72	79.25	E.	13	E.-SE.-E.	−14	Very steady.
	.04	20.73	79.23					
Aug. 6	.04	20.70	79.26	S.	11	S.-SW.-S.	−40	Strong rise.
	.03	20.69	79.28					
Summer-1940:								
Dec. 31	.09	20.50	79.41	W.	4	W.-NW.-W.	+28	Rising slowly.
	.09	20.50	79.41					
31*	.08	20.49	79.43	NW.	6	W.-NW.-W.	+29	Rising slow.
	.06	20.50	79.42					
1941:								
Jan. 2	.17	20.53	79.30	NE.	16	E.-NE.-E.	+32	Steady.
	.15	20.49	79.36					
4	.11	20.59	79.30	SE.	9	E.-SE.-S.	+24	Falling slowly.
	.09	20.58	79.33					
5	.04	20.54	79.42	SE.	10	SE.	+20	Steady.
	.02	20.53	79.45					
	.06	20.48	79.46					
5*	.06	20.52	79.42	SE.	9	SE.	+18	Steady.
	.07	20.53	79.40					
6	.16	20.55	79.29	SW.	6	SW.-S.-SW.	+22	Strong fall.
	.14	20.57	79.29					
Jan. 12	.05	20.58	79.37	SW.	14	SW.-S.-SW.	+25	End of rise.
	.07	20.59	79.38					
15	.03	20.63	79.34	SE.	14	E.-SE.	+16	Falling.
	.06	20.63	79.31					
16	.09	20.56	79.34	SE.	12	SE.	+18	End of fall.
	.09	20.56	79.34					
18	.06	20.60	79.34	E.	7	S-SE.-E.	+12	Steady.
	.06	20.60	79.34					
18*	.07	20.60	79.33	SE.	9	S.-E.-SE.	+12	Steady.
	.06	20.64	79.30					

*Different samples on the same day.

DISCUSSION

In view of the fact that the results obtained in this study are so divergent from those presented by Benedict (**1**) and Carpenter (**3**), which are to be considered as standards for atmosphere in temperate climates below the tropopause, some discussion of any possible errors in the determinations is necessary.

The apparatus itself is one that has been in constant use over a period of years in the Fatigue Laboratory at Harvard University and also on several field trips throughout the country. Results obtained with it have always been above criticism. Unfortunately, no check determinations on "standard" middle latitude air were made with the apparatus. The air analysis program was not planned until the expedition was in the Antarctic, so no samples were taken along for comparison. After the results had been obtained it was planned to make a series of readings whenever the ship was moored during the northward voyage home, but before these could be begun the Haldane apparatus was rendered inoperative during a severe storm.

The reagents used were of the highest quality and absorbents prepared from them exactly according to the procedures recommended by Peters and van Slyke. Any decrease in the efficiency of the reagents, especially the potassium pyrogallate, was readily noted as a sluggishness in absorption and a failure to give constant results within a prescribed time. Whenever such an occasion arose, the old reagents were replaced by fresh ones.

Leaks in the apparatus, which occurred occasionally, were easily detected because of inconstancy of readings and failure to obtain check results on a given sample. These were immediately eliminated by removal, cleaning and regreasing of all stopcocks. The apparatus was then tested according to the prescribed procedure.

Contamination of the sample during transfer from the sample bottle to the measuring burette is impossible. After the sample is in the apparatus, the possible effect of changes in external conditions is eliminated. In short, unless the apparatus is clean, all capillary tubing and stopcocks free for the passage of gas, the reagents in good condition and the proper routine followed, check results are impossible.

All of the determinations were done in duplicate at least, and separate analyses of the same sample were taken as data for this report only when they agreed within the experimental limits of error of the apparatus, which are 0.03 percent for carbon dioxide and 0.04 percent for oxygen. Consequently, the apparent deficiency of oxygen in the Antarctic atmosphere is considered to be real.

SUMMARY

Analyses of the lower atmosphere of the Antarctic were made using the Haldane portable apparatus. A variable deficiency in the oxygen content of the air, too great to be attributable to instrumental error, was found. The values for oxygen range from 20.76 to 20.48 volume percent. Since all possible sources of error were eliminated, the deficiency is considered to be real.

ACKNOWLEDGMENTS

To Dr. Martin Shepherd of the National Bureau of Standards is due the original suggestion that the analyses be made. He requested that 10 special air-sample flasks be filled in the Antarctic and returned to him. These flasks were taken along and duly filled at the expedition's East Base, in Palmer Land, 800 miles south of Cape Horn, but were abandoned there together with all other equipment when ice conditions forced evacuation of all personnel at that base by airplane. The analyses here given were made at West Base, 1,400 miles away, independently of the original program.

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Publication of this report has been approved by the U. S. Antarctic Service.

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METEOROLOGICAL AND CLIMATOLOGICAL DATA FOR MAY 1942

[Climate and Crop Weather Division, J. B. KINCER, in charge]

AEROLOGICAL OBSERVATIONS

TABLE 1.—*Mean free-air barometric pressure in millibars, temperature in degrees Centigrade, and relative humidities in percent, obtained by airplanes and radiosondes during May 1942*

Altitude (meters) m. s. l.	Albuquerque, N. Mex. (1,620 m.)				Atlanta, Ga. (300 m.)				Bismarck, N. Dak (505 m.)				Boise, Idaho (864 m.)				Brownsville, Tex. (6 m.)				Buffalo, N. Y. (221 m.)			
	Number of observations	Pressure	Temperature	Relative humidity	Number of observations	Pressure	Temperature	Relative humidity	Number of observations	Pressure	Temperature	Relative humidity	Number of observations	Pressure	Temperature	Relative humidity	Number of observations	Pressure	Temperature	Relative humidity	Number of observations	Pressure	Temperature	Relative humidity
Surface	31	834	19.3	18	31	982	19.1	75	31	955	10.1	74	31	914	11.8	64	30	1012	24.4	85	31	990	13.1	82
500					31	960	20.1	64									30	957	21.8	89	31	958	13.8	72
1,000					31	906	17.1	64	31	900	8.6	70	31	899	12.7	60	30	904	20.9	65	31	902	11.8	71
1,500					31	854	13.3	68	31	847	5.7	71	31	847	10.3	55	30	853	19.8	53	31	850	9.0	75
2,000	31	798	18.8	17	31	804	9.9	70	31	796	3.3	72	31	797	6.4	56	30	804	17.1	47	31	800	6.5	72
2,500	31	752	15.0	17	31	757	7.0	65	31	748	0.6	70	31	749	2.4	60	30	758	14.4	41	31	752	4.0	68
3,000	31	709	10.6	18	31	712	3.9	60	31	703	−1.9	67	31	704	−1.2	63	30	714	11.4	41	31	707	1.5	65
4,000	31	628	2.1	19	30	630	−0.7	47	30	619	−7.5	58	31	620	−8.5	67	30	633	5.3	37	31	624	−4.1	61
5,000	31	554	−6.6	21	30	555	−7.2	42	30	544	−14.1	53	31	544	−15.3	63	29	560	−1.7	38	31	549	−10.4	57
6,000	31	486	−14.5	23	29	487	−14.3	40	30	476	−21.3	52	30	476	−22.5	62	29	493	−8.5	37	31	482	−16.8	53
7,000	31	425	−21.6	23	29	426	−21.2	39	30	414	−28.8	50	29	414	−29.8	62	28	433	−15.3	35	31	421	−23.9	51
8,000	31	370	−28.8	22	29	372	−28.2	38	30	359	−36.9	49	29	359	−37.1	59	28	378	−22.1	35	31	366	−31.2	50
9,000	30	322	−36.3		29	322	−35.5	38	29	310	−44.7		29	310	−43.8		27	329	−29.3	35	31	317	−38.8	49
10,000	30	278	−43.7		28	279	−42.9		29	266	−51.3		29	267	−49.0		27	286	−36.8	35	29	274	−46.2	
11,000	29	239	−50.6		28	240	−49.8		29	228	−54.4		29	229	−52.5		27	247	−44.5		29	235	−52.2	
12,000	29	204	−56.2		28	206	−55.8		27	195	−55.3		29	196	−53.9		25	212	−52.1		27	201	−57.7	
13,000	29	174	−59.4		28	175	−60.6		27	166	−55.0		28	167	−54.0		24	182	−58.8		27	171	−60.3	
14,000	28	148	−61.0		28	149	−61.7		25	142	−54.4		26	143	−54.0		24	154	−64.9		27	145	−60.7	
15,000	27	126	−61.7		28	127	−61.9		22	122	−55.1		24	122	−54.6		20	131	−70.0		23	124	−59.2	
16,000	25	108	−63.0		28	108	−62.5		18	104	−56.0		22	105	−55.2		20	111	−73.3		23	106	−59.2	
17,000	20	91	−62.6		28	92	−63.0		13	89	−55.7		16	89	−55.9		15	93	−75.8		18	90	−58.5	
18,000	11	77	−61.8		22	78	−62.2		9	76	−54.9		9	76	−56.1		12	78	−74.6		11	76	−58.1	
19,000	7	66	−60.3		14	66	−60.7										9	66	−71.4					
20,000					5	56	−59.1										5	56	−67.9					